

NASA Technical Memorandum 81824

(NASA-TM-81824) HIGH-TEMPERATURE ADHESIVES
FOR BONDING POLYIMIDE FILM (NASA) 28 F
HC A03/MF A01 CSCL 11A

N80-26449

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HIGH-TEMPERATURE ADHESIVES FOR BONDING POLYIMIDE FILM

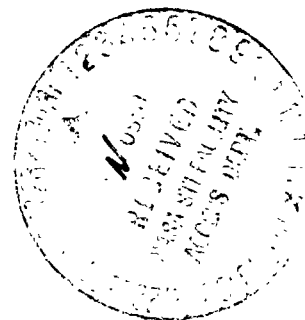
Anne K. St. Clair, Wayne S. Slemp, and
Terry L. St. Clair

May 1980



National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23665



Very few adhesives exist that are suitable for long-term use at elevated temperature. Commercially available high-temperature adhesives have been formulated for bonding metals such as steel and titanium. However, these systems generally contain additives which make the resins too brittle for film bonding applications. A particular need for adhesives that are compatible with polyimide film was recently presented by the proposed NASA Solar Sail Program.

The spinning sail shown in Figure 1 was intended originally for a rendezvous mission with Halley's Comet in 1986, following a launch in November 1981. Had the program continued, an adhesive would have been needed to join strips of $0.002\mu\text{m}$ (.08 mil) ultrathin film at intervals across each blade measuring 8m in width by 7350m in length.

For such an application on any future large space structure, the adhesive used for bonding thin film will have to form a flexible coating and be amenable to bonding cycles which involve low pressure and very short time at the bonding temperature. The objective of this work was to develop and evaluate a high-temperature adhesive for DuPont's ultrathin Kapton[®] H film which could provide good performance in a space environment for long term at 575K.

Linear condensation polyimides are a group of high-temperature polymers which show promise as adhesives and possess the capability of forming flexible film coatings. In addition, they should have good compatibility with linear polyimide Kapton film adherends. Three

promising polyimide LaRC adhesives (1,2) prepared in the amic acid form in the aliphatic ether solvent, diglyme, were developed and studied along with a new experimental NR-150-B2X (3,4) precursor adhesive prepared in amide solvent as a monomeric mixture.

EXPERIMENTAL

Adhesives

The monomers used in the preparation of the LaRC adhesives were 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA), and 3,3'- or 4,4'-diaminobenzophenone (DABP). The BTDA and PMDA were obtained commercially and purified by vacuum sublimation (m.p. 497K and 558K, respectively). The diamines were obtained from commercial sources and purified by recrystallization. The reagent grade bis (2-methoxyethyl) ether (diglyme) was used as received.

The general reaction scheme followed in the preparation of LaRC adhesives is shown in Figure 2. The LaRC-2 polyamic acid was prepared by reacting stoichiometric amounts of 3,3'-DABP (0.015 mole) and BTDA (0.015 mole) in 45g of diglyme at ambient temperature for 16 hours. In a similar manner, the amic acid of LaRC-3 was made by adding a 2:1 molar ratio of BTDA (0.010 mole)/PMDA (0.005 mole) to 3,3'-DABP (0.015 mole) in 42g of diglyme. The amic acid of LaRC-4 was prepared from a 3:1 ratio of BTDA (0.012 mole)/PMDA (0.004 mole) and 4,4'-DABP (0.016 mole) in 46g of diglyme.

Films were cast from the 15 percent solids amic acid solutions onto soda-lime glass plates and thermally cured by heating in a forced air oven for one hour at each of three temperatures, 373K,

473K, and 573K. The LARC polyimide films formed in this manner were then characterized. The remaining polyamic acid solutions were kept under refrigeration until needed for bonding. The experimental NR-150 precursor adhesive solution, NR-150-B2X, was obtained as a mixture of monomers at 48 percent solids (w/w) in N-methylpyrrolidone (NMP) (5). The monomeric binder solution contained a 1.5 percent excess of the 2,2-bis-(3',4'-dicarboxyphenyl)-hexafluoropropane dianhydride (6F) and a 3:2 ratio of para-phenylenediamine (PPD)/oxydianiline (ODA). The experimental NR-150-B2X solution was diluted from 48 percent to 32 percent with ethanol before coating adherends. A film of the monomeric NR-150-B2X solution was also cast from NMP/ethanol, cured, and characterized.

Characterization

Inherent viscosities of the LARC resins were determined at a concentration of 0.5 percent in dimethylacetamide at 308K. The glass transition temperature (T_g) of each polyimide film was determined by differential scanning calorimetry (DSC) on a DuPont Model 990 Thermal Analyzer with the Standard DSC Cell Attachment at a heating rate of 20K/min. The T_g values of the adhesive bondlines were measured by thermomechanical analysis (TMA) in static air at a 5K/min. heating rate on a DuPont Model 943 Thermomechanical Analyzer. A 1/2 cm by 1/2 cm sample was cut from the adhesive bondline and mounted under the TMA quartz penetration probe loaded with a 20g weight.

Adherends

The polyimide Kapton adherends were acquired from the Electrical Insulation Products Division, E. I. du Pont de Nemours and Co.,

in the following thicknesses; 0.025 mm (1 mil), 0.051 mm (2 mil), 0.076 mm (3 mil), and 0.127 mm (5 mil). Kapton panels measuring 11.4 cm (4.5 in) by 15 cm (6 in) were cut from the film rolls with the 15-cm dimension in the longitudinal direction. No surface preparation of the film was required other than the removal of fingerprints and dust with ethanol when necessary. The tensile properties of the Kapton adherends were obtained on film strips 2.54 cm (1 in) wide and are shown in Table 1. The majority of adhesive screening was performed with the 0.051 mm (2 mil) Kapton. Whenever bonding with the thinner Kapton was attempted, 50 percent of the failures occurred in the adherend, not the adhesive bondline. Therefore, to obtain consistent adhesive strengths, films 0.051 mm (2 mil) or thicker were bonded.

Bonding Process

Kapton film panels were brush coated 0.64 cm (1/4 in) from the edge with either the LARC polyamic acid solutions in diglyme or the NR-150-B2X in NMP/ethanol. The coated adherends were B-staged 1 hour at 373K and 1/2 hour at 448K in a forced air oven. Each primed panel was then overlapped 0.64 cm (1/4 in) with an unprimed panel and bonded at 616K (650°F) with a hot iron for 20 seconds. Only contact pressure of the iron on the bondline was necessary for bonding. Final bondline thicknesses ranged from 0.008 mm (0.3 mil) to 0.013 mm (0.5 mil).

Vacuum Aging

Prior to vacuum aging, each bonded film specimen was cut into four 2.54 cm (1 in) strips; and a small hole was punched at the top

TABLE I - MECHANICAL PROPERTY DATA ON KAPTON ADHERENDS

Adherend Thickness	Test Temperature	Tensile Strength MPa (psi)	Yield Strength at 2% MPa (psi)	Elongation %	Tensile Modulus MPa (psi)
0.025 mm (1 mil)	RT	172 (24,900)	62 (9000)	35	2920 (424,000)
	575K	78 (11,300)	31 (4500)	55	1230 (179,000)
0.051 mm (2 mil)	RT	177 (25,700)	44 (6400)	84	2760 (400,600)
	575K	63 (9200)	24 (3500)	70	1040 (150,600)
0.076 mm (3 mil)	RT	163 (23,700)	50 (7200)	57	2500 (362,000)
	575K	71 (10,300)	26 (3700)	82	1120 (162,000)
0.127 mm (5 mil)	RT	179 (26,000)	50 (7300)	56	2890 (419,000)
	575K	74 (10,700)	26 (3800)	82	1350 (196,000)

of each panel for mounting in the vacuum oven (Figure 3). Sets of specimens were aged isothermally at 575K in vacuum and removed for testing after 250, 500, 1000, 1500, 2000, 3000, and 6000 hours. Samples were mounted on metal racks at the center, from front to rear, of a vacuum chamber having a 76.2-cm (30-in) diameter and equipped with an ion gauge and trapped diffusion pump. Throughout the experiment, a vacuum of 670 μ Pa to 1870 μ Pa, gauge (2×10^{-7} in to 5.5×10^{-7} in Hg) was maintained. Three independent and prepositioned thermocouples monitored the chamber temperatures at all times.

Testing

Tensile tests of the Kapton adherends and lap-shear tests of adhesively bonded Kapton films were performed on an Instron Universal Testing Instrument Model TT-6 according to ASTM Designation D882-61T. Specimens were tested at a cross-head speed of 0.51 cm (0.2 in)/min using a gauge length of 7.62 cm (3 in). Elevated temperature testing at 575K was conducted in an Instron Environmental Chamber wherein each specimen was soaked for 10 minutes at the temperature before testing.

Resin Properties

The polyimide resins used in this investigation and some of their properties are listed in Table II. The LARC resins, made by reacting DABP with the appropriate dianhydride monomers in diglyme at 15 percent solids (w/w), yielded high-molecular-weight polyamic acids as indicated by the inherent viscosities (η_{inh}). Films cast from the LARC amic acid solutions and cured at 573K were clear

yellow and flexible. Glass transition temperatures of the polyimide films as determined by DSC ranged from 520K (477°F) for LARC-2 to 570K (567°F) for LARC-4. A film made from the monomeric NMP/ethanol solution of NR-150-B2X and cured to 573K was clear purple and brittle, but self-supporting. The T_g of this material was found to be 595K (612°F) by DSC, compared to 596K (613°F) reported by DuPont (5). Dynamic TGA curves of the polyimide films cured at 573K in air are presented in Figure 4. LARC-2 and LARC-3, which possessed the lower T_g values, were the most thermally stable when heated in a nitrogen atmosphere. Isothermal TGA curves of the polyimide films aged at 575K in nitrogen are shown in Figure 5. The adhesives displayed excellent thermal stability with losses between 1.0 percent for LARC-4 and 4.5 percent for LARC-3 after 500 hours at 575K.

TABLE II - PROPERTIES OF ADHESIVES			
Resin	Formulation	Amic Acid η_{inh}	T_g K (°F)
LARC-2	BTDA 3,3'-DABP	0.70	520 (477)
LARC-3	2 BTDA/1 PMDA 3,3'-DABP	0.63	542 (516)
LARC-4	3 BTDA/1 PMDA 4,4'-DABP	0.50	570 (567)
NR-150-B2X	6F(1.5% excess) 3 PPD/2 ODA	--	595 (612)

Bonding Conditions

A schematic of the bonded film specimens is shown in Figure 6. The procedure developed for bonding thin Kapton film using any of the LARC adhesives or NR-150-B2X has demonstrated excellent feasibility for large-scale bonding. Kapton film as thick as 0.127 mm (5 mil) was bonded in 20 seconds at 616K (650°F) with only the contact pressure of a small iron used as a heat source. The 0.64 cm (1/4 in) overlap of the Kapton bondlines allowed an easy escape for any volatiles and yielded bondlines that were relatively void-free. In addition, there was little or no adhesive flash evolved during the bonding of the LARC or NR-150-B2X materials. This indicated that the B-stage prior to bonding allowed adequate but not an excessive amount of flow. The overall bonding procedure was facile and economical, both of which are desirable attributes for bonding thin film for future large space structures.

In particular, the LARC adhesive materials proved advantageous because the non-toxic diglyme used as a solvent for these adhesives was readily removed during the bonding procedure. An additional advantage exhibited by the LARC resins was that LARC-2, LARC-3, and LARC-4 formed clear, flexible, self-supporting films when cast from diglyme in the polyamic acid form and B-staged to 448K (347°F). Therefore, these materials could be supplied in the form of a film tape, which would eliminate working with a solvent and facilitate bonding.

Kapton/Kapton Bond Strength

Results from the room temperature and elevated temperature lap-shear tests of LARC-2, LARC-3, LARC-4, and NR-150-B2X Kapton/Kapton bonds are shown in Figure 7. Each data point represents the average lap-shear strength of eight individual specimens. Average deviations from the mean values ranged from 68 kPa (10 psi) at RT and 41 kPa (6 psi) at elevated temperatures for the LARC adhesive specimens to 96 kPa (14 psi) at RT and 37 kPa (5.4 psi) at elevated temperatures for the NR-150-B2X specimens. The average deviation for NR-150-B2X lap-shear specimens at 575K was 61 percent less than the deviation at RT. Failure in all cases occurred in the adhesive. Percent retention of room temperature lap-shear strengths at elevated temperature were as follows:

- o 27 percent at 575K (575°F)
and 28 percent at 589K
(600°F) for LARC-2 specimens
- o 33 percent at 575K (575°F)
and 21 percent at 589K
(600°F) for LARC-3 specimens
- o 49 percent 575K (575°F) and
53 percent at 589K (600°F) for
LARC-4 specimens
- o 56 percent at 575K (575°F) for
NR-150-B2X specimens.

At 575K, the materials possessing the higher T_g values retained RT properties better than those with the lower T_g values (Table II). LARC-4 and NR-150-B2X possessing the higher T_g values in the range of the test temperature displayed the greatest retention in strength.

The effect of adherend thickness on lap-shear strength is presented in Figure 8 for LARC-3 Kapton/Kapton bonds. RT strength was found to be dependent upon the thickness of the adherends. Failure for all bonds occurred in the adhesive except for those specimens bonded with the thinner 0.025 mm (1 mil) Kapton adherends. Fifty percent of the failures of the 0.025 mm Kapton specimens were attributed to the adhesive and 50 percent to the adherend. (See Figure 3.) For these particular thin film joints, the adhesive was as strong as or, in some cases, stronger than the film to which it was bonded.

Isothermal aging of lap-shear specimens comprised of LARC and NR-150-B2X adhesives bonded to 0.051 mm (2 mil) Kapton was performed in vacuum at 575K. After aging between 500 and 1000 hours, both the bondlines and adherends darkened. Room temperature lap-shear strengths of the bondlines obtained after 0, 250, 500, 1000, 1500, 2000, 3000 and 6000 hours of vacuum aging are shown in Figure 9a. RT strengths of all of the adhesives peaked at 500 hours, indicative of a post-curing effect. After 3000 hours of aging at 575K, the RT strengths of all four adhesives were still increasing, probably due to a gradual crosslinking of the polymer systems. Somewhere between 3000 and 6000 hours

aging, the Kapton bonds began to lose RT strength. With the exception of LARC-3, however, the decline in strength after 6000 hours was minimal.

Figure 9b shows the lap-shear data for the specimens aged at 575K in vacuum and tested at 575K. All adhesives tested at elevated temperature increased in strength while aging for the first 1000 hours. After 1000 hours, the strength of NR-150-B2X had reached approximately 620 kPa (90 psi) which was the highest lap-shear strength obtained for any of the adhesives tested at elevated temperature. The higher strength of NR-150-B2X at 575K was probably due to the higher T_g of this material. The strength of LARC-4 specimens, however, changed the least from 0 to 6000 hours aging. All four adhesive systems exhibited excellent retention of elevated-temperature strength after aging 6000 hours at 575K.

TMA was used to measure the T_g values of the actual adhesive Kapton/Kapton bondlines before and after aging in vacuum at 575K. Figure 10 shows a plot of T_g versus time at 575K where each symbol represents an average of four data points. After aging for 500 hours, all adhesives had reached the T_g s determined previously for the fully cured polymers by DSC (Table 1). Between 1000 and 3000 hours, T_g values of NR-150-B2X and LARC-4 remained constant, but those values obtained for LARC-2 and LARC-3 were still increasing. With the exception of LARC-3, the T_g values of all other adhesive bondlines gradually increased after aging 3000 to 6000 hours.

Examples of TMA curves obtained from 1 cm X 1 cm samples cut from the adhesive bonds are presented in Figure 11. The LARC-3 curves, which are representative of the LARC adhesive series, showed an increase in T_g from 520K (477°F) to 571K (568°F) on aging 3000 hours, but no significant change in the amount of probe displacement, 5 μ m (0.19 mil). The T_g of NR-150-B2X specimens also rose from 550K (531°F) at 0 hours to 616K (649°F) after 3000 hours. Unlike LARC-3, the probe displacement for NR-150-B2X bondlines was 96 percent less after aging [from 51 μ (2.0 mil) to 2 μ m (0.08 mil)]. Such behavior of the NR-150-B2X curve at 0 hours aging demonstrates the plasticizing of this material due to residual NMP solvent. Upon curing at elevated temperature, the solvent is then removed. Therefore, the bonding process used for this adhesive was not sufficient for complete solvent removal. This ability of NMP to remain attached to the NR-150 polymers and other polyimides well over its boiling-point temperature has been recognized previously. Whether or not the presence of NMP in the NR-150-B2X Kapton/Kapton bondline is detrimental has not been proven at this time.

Conclusions

Four experimental polyimide materials covering a 75K (135°F) range in T_g have been developed as high-temperature adhesives for bonding Kapton film. A unique bonding process requiring only 20 seconds at the bonding temperature and minimal pressure was developed which shows promise for the large scale bonding of thin Kapton sheet film for future large space structures. All four of the candidate polyimides show excellent potential as adhesives

for Kapton bonding. NR-150-B2X and LARC-4, the materials characterized by the higher T_g s, exhibited the best retention of properties on long-term aging at elevated temperature in vacuum. The main advantage offered by the LARC adhesives is that these materials can be supplied in the form of a flexible tape already B-staged and ready for instant bonding. In addition, the non-toxic ether solvent, diglyme, from which the LARC resins were prepared, was easily removed on bonding. This disallowed any plasticization of the polymers by solvent, as was observed with NR-150-B2X. The relatively simple bonding process and the ease in handling make these adhesives attractive for use in bonding Kapton film.

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Figure 1. NASA Heliogyro Solar Sail.

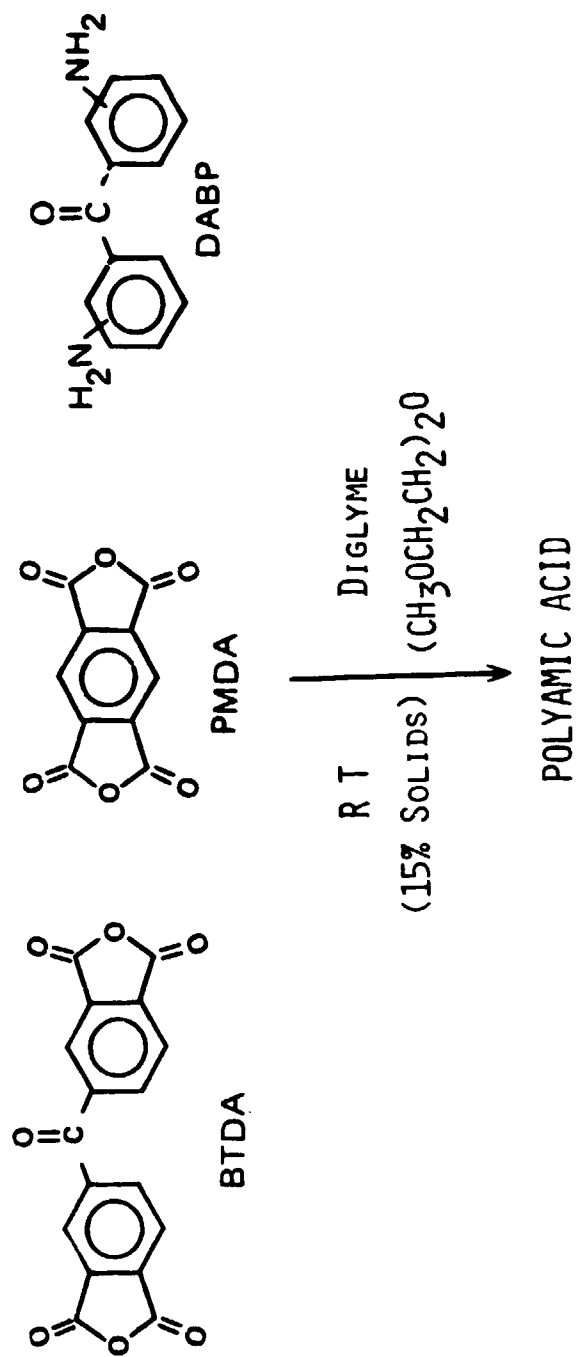


Figure 2. LARC adhesive chemistry.

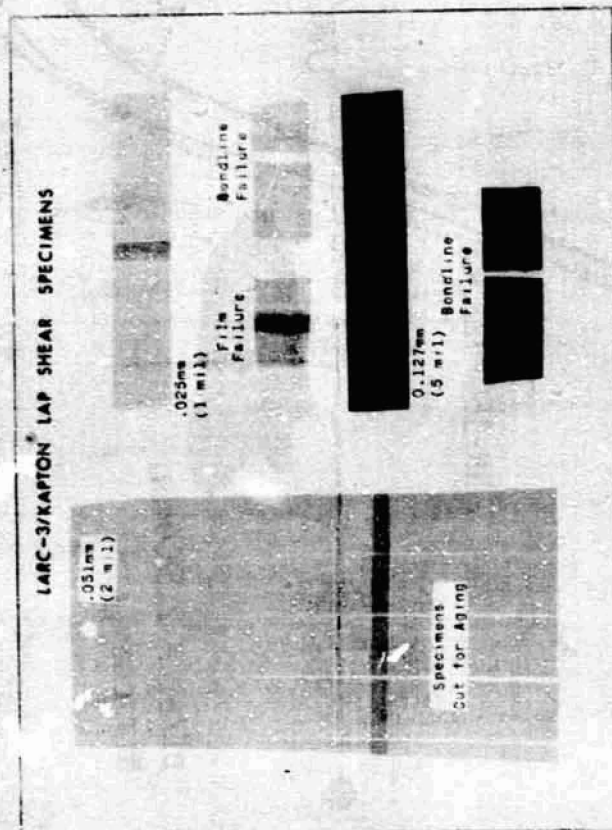


Figure 3. Film specimens before and after testing.

THERMOGRAMS OF AIR CURED POLYIMIDE FILMS

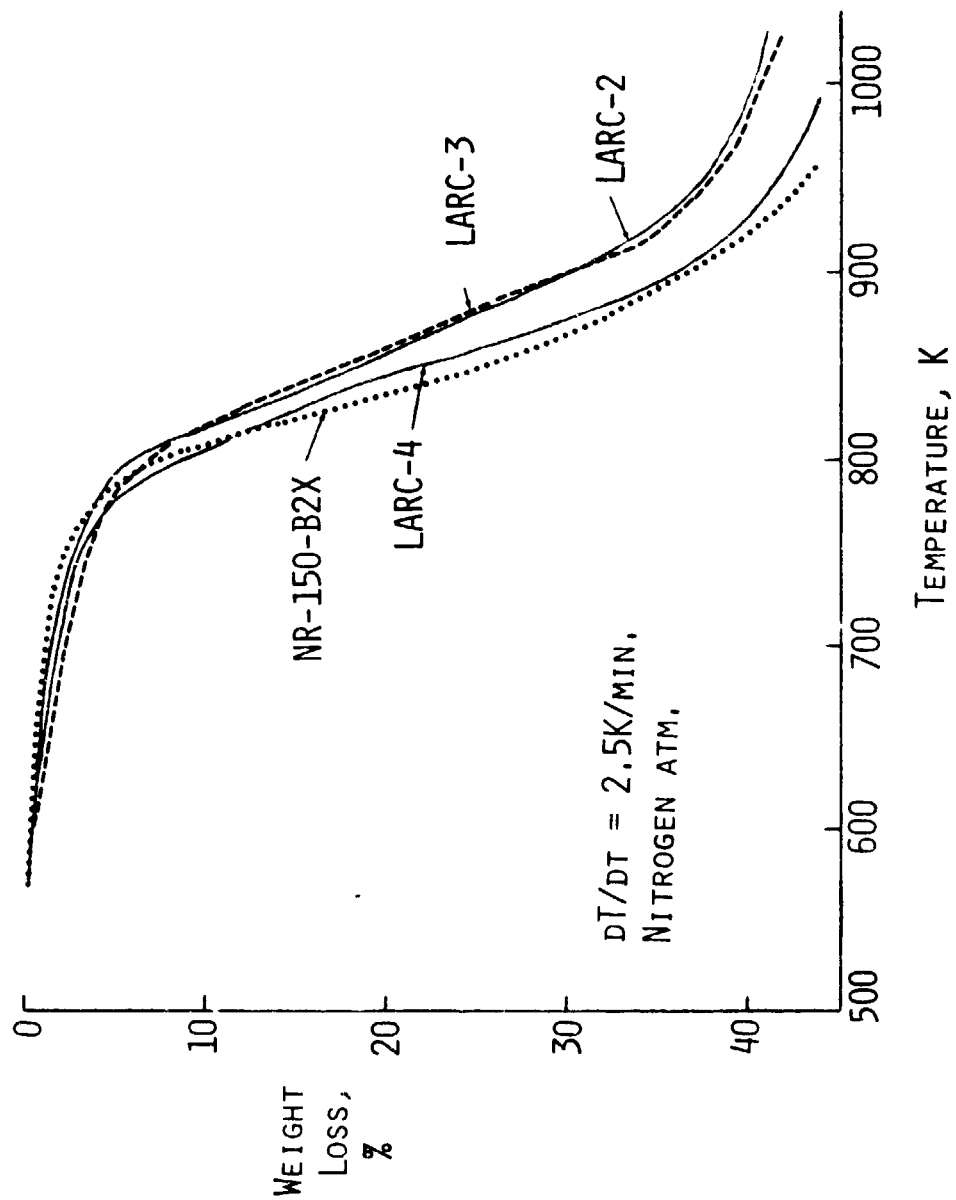


Figure 4. Thermograms of films cured at 573K in air.

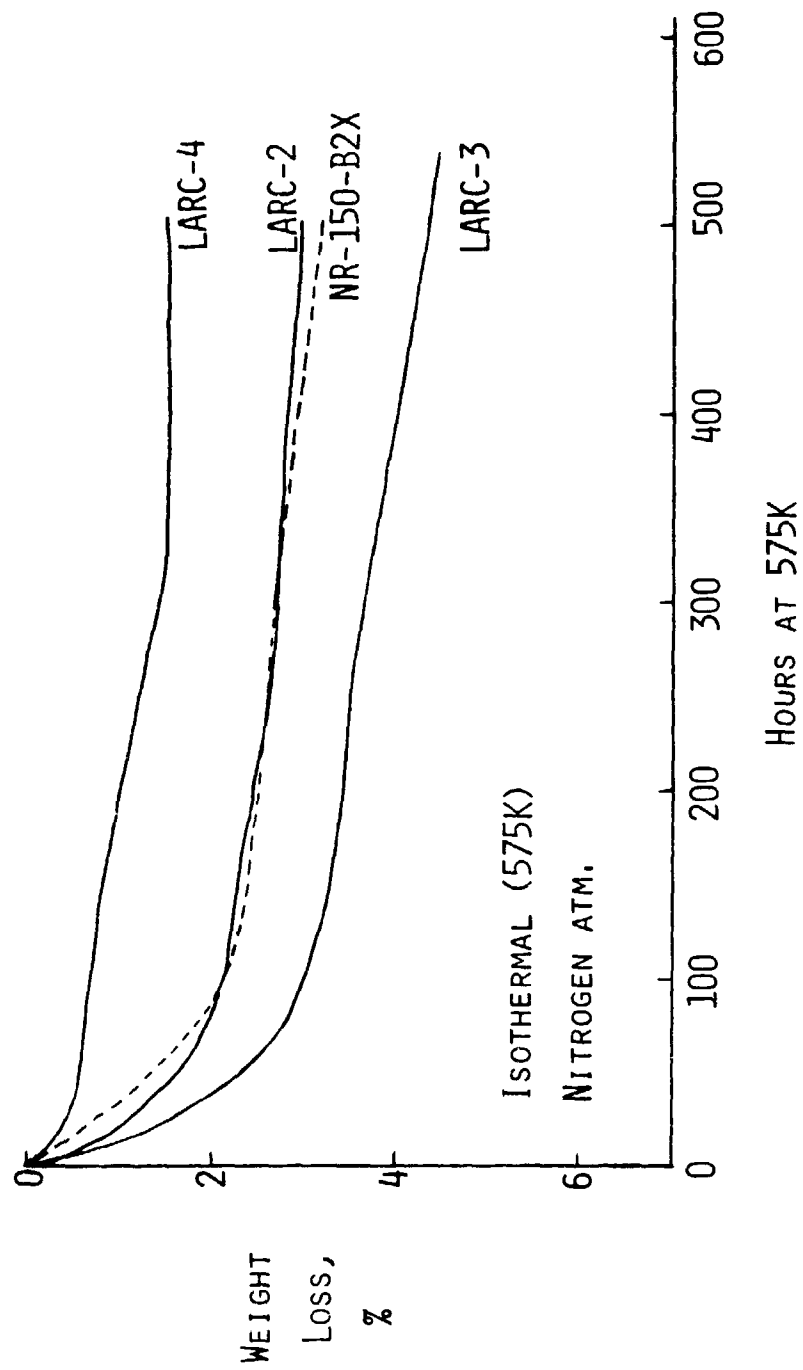


Figure 5. Isothermal TGAs of polyimide films cured at 573K in air.

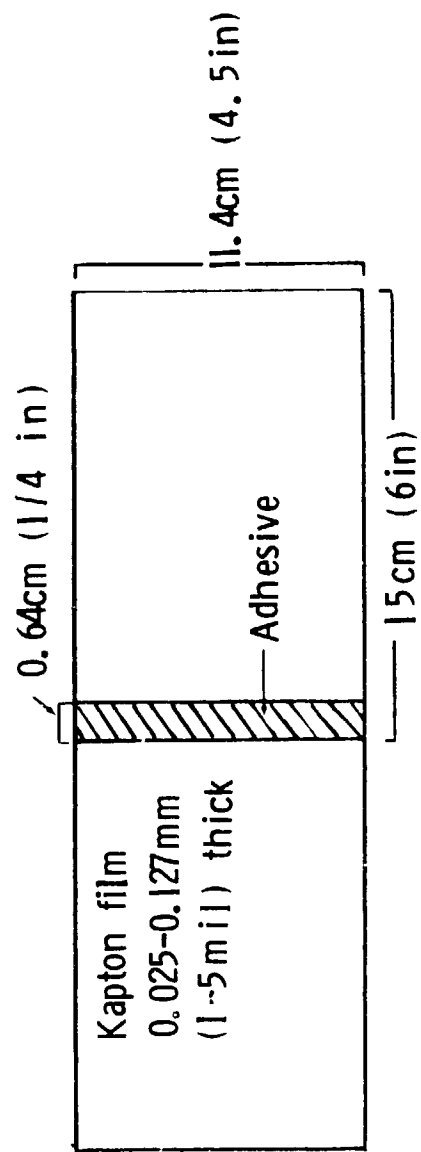


Figure 6. Schematic of bonded film specimens.

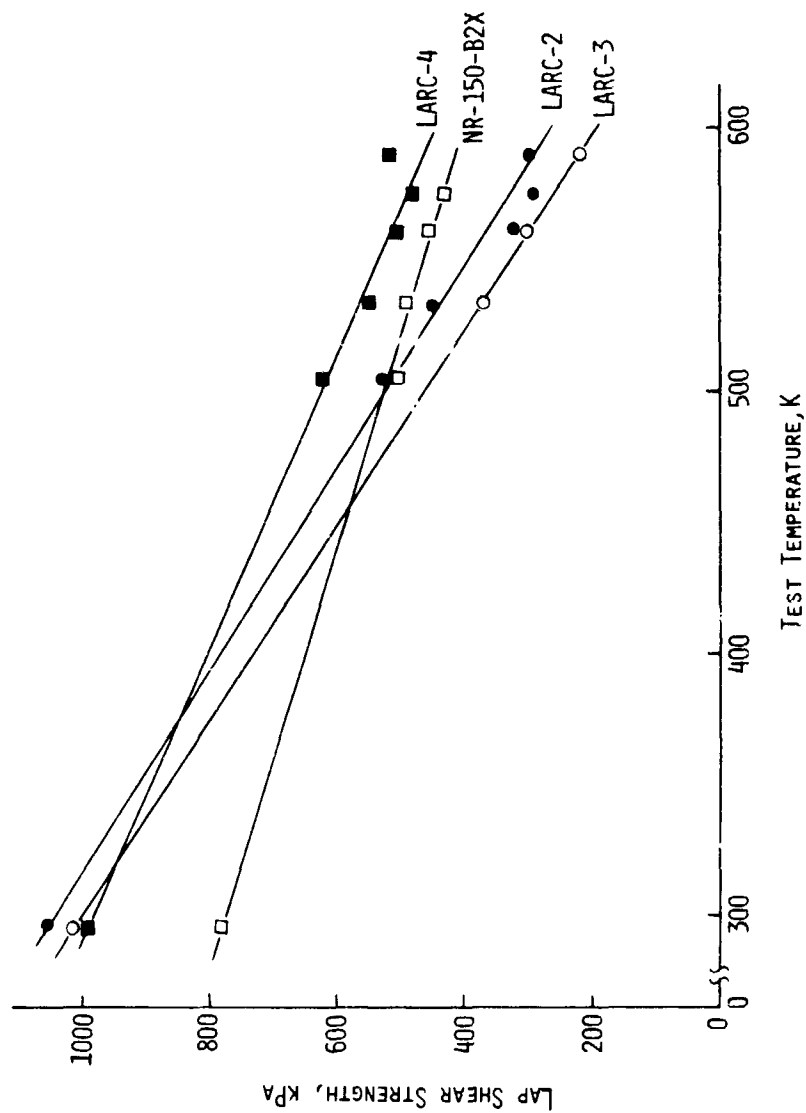


Figure 7. Lap-shear strength of 0.051mm (2 mil) Kapton bonds versus temperature.

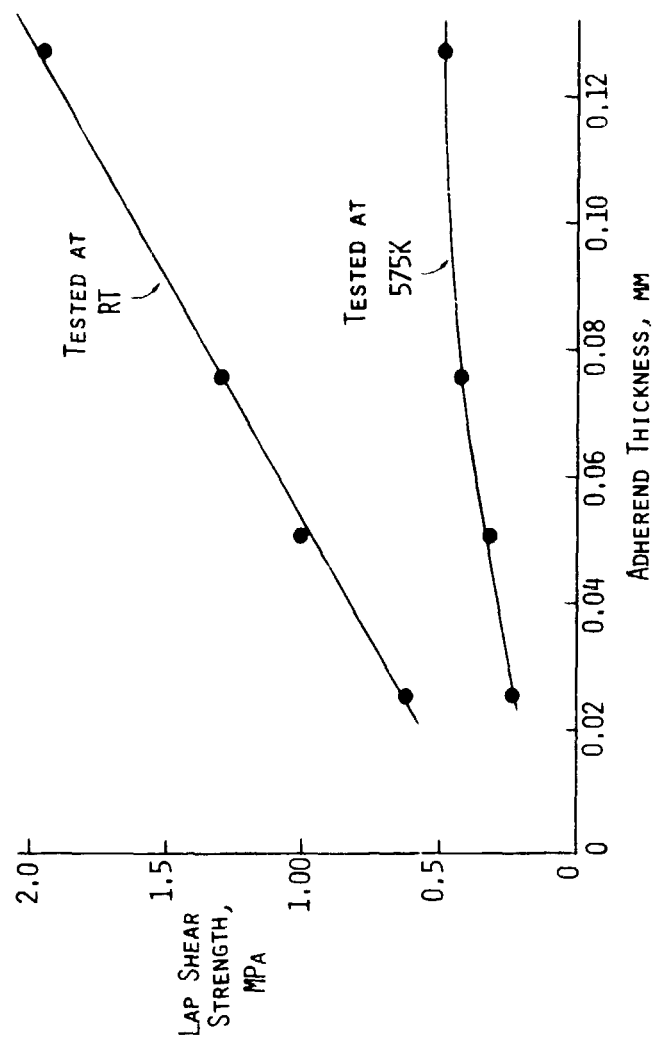


Figure 8. Room- and elevated-temperature lap-shear strengths of LARC-3 bonded to Kapton of varying thicknesses.

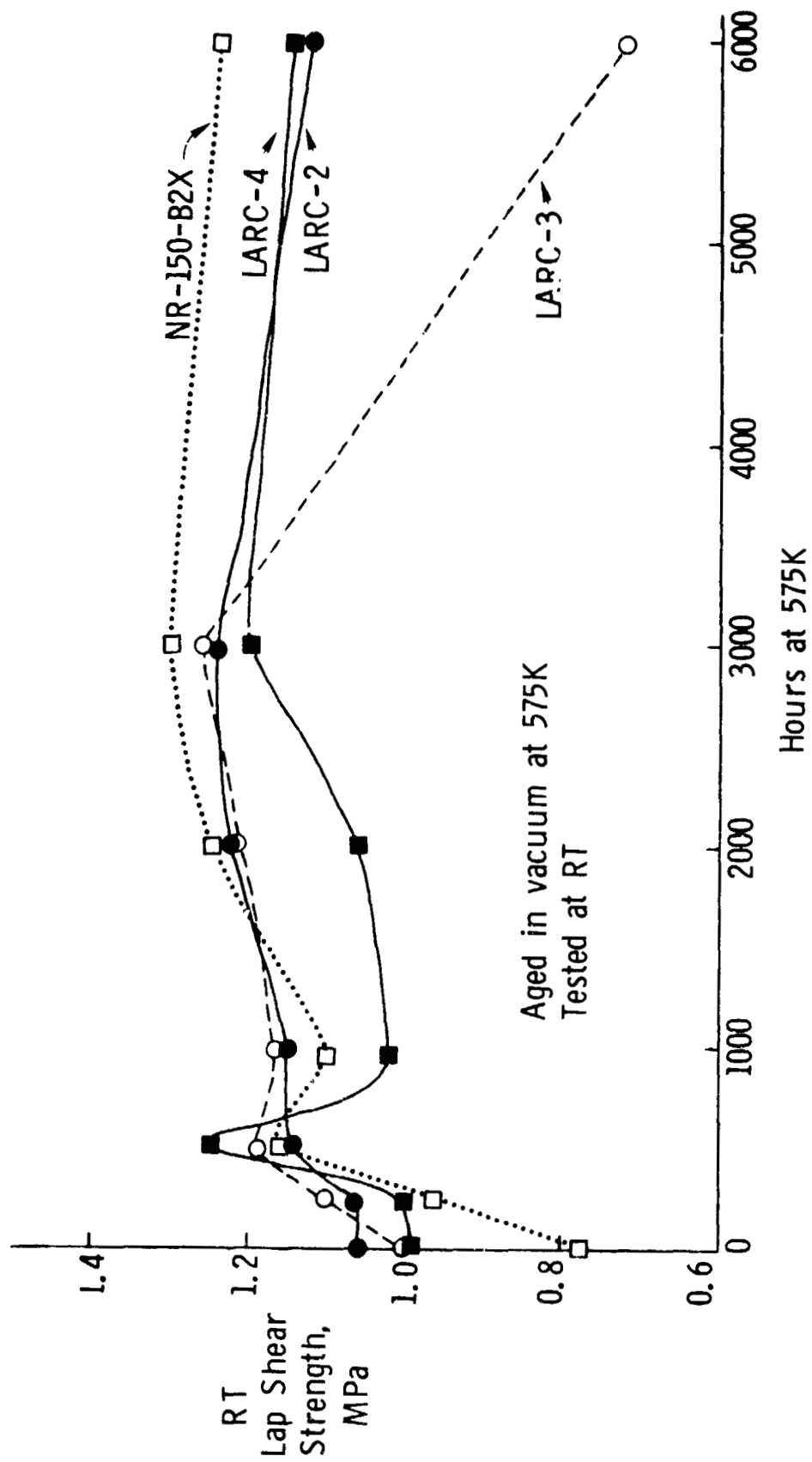


Figure 9a. Room-temperature lap-shear strengths of Kapton aged at 575K in vacuum.

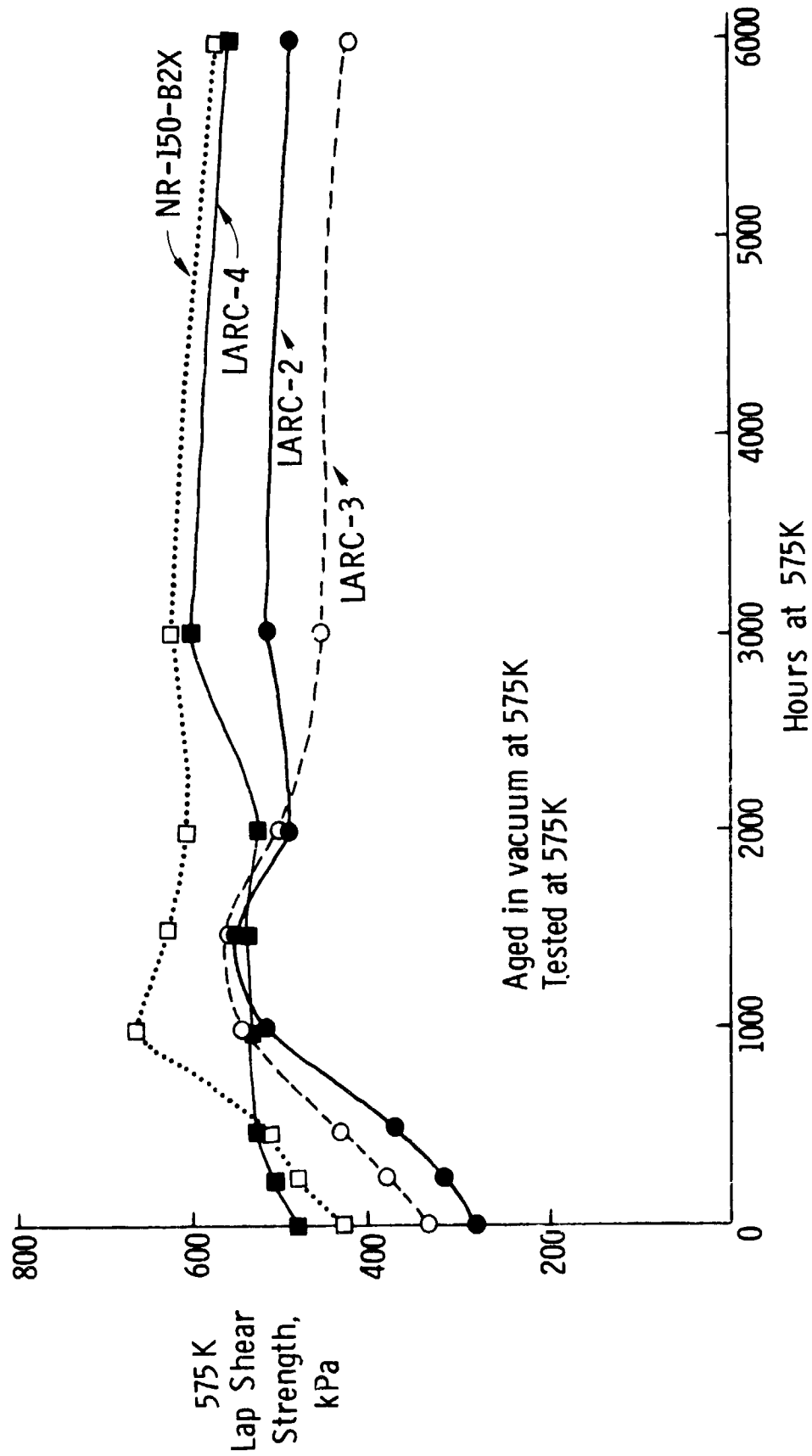


Figure 9b. Elevated-temperature lap-shear strengths of Kapton aged at 575K in vacuum.

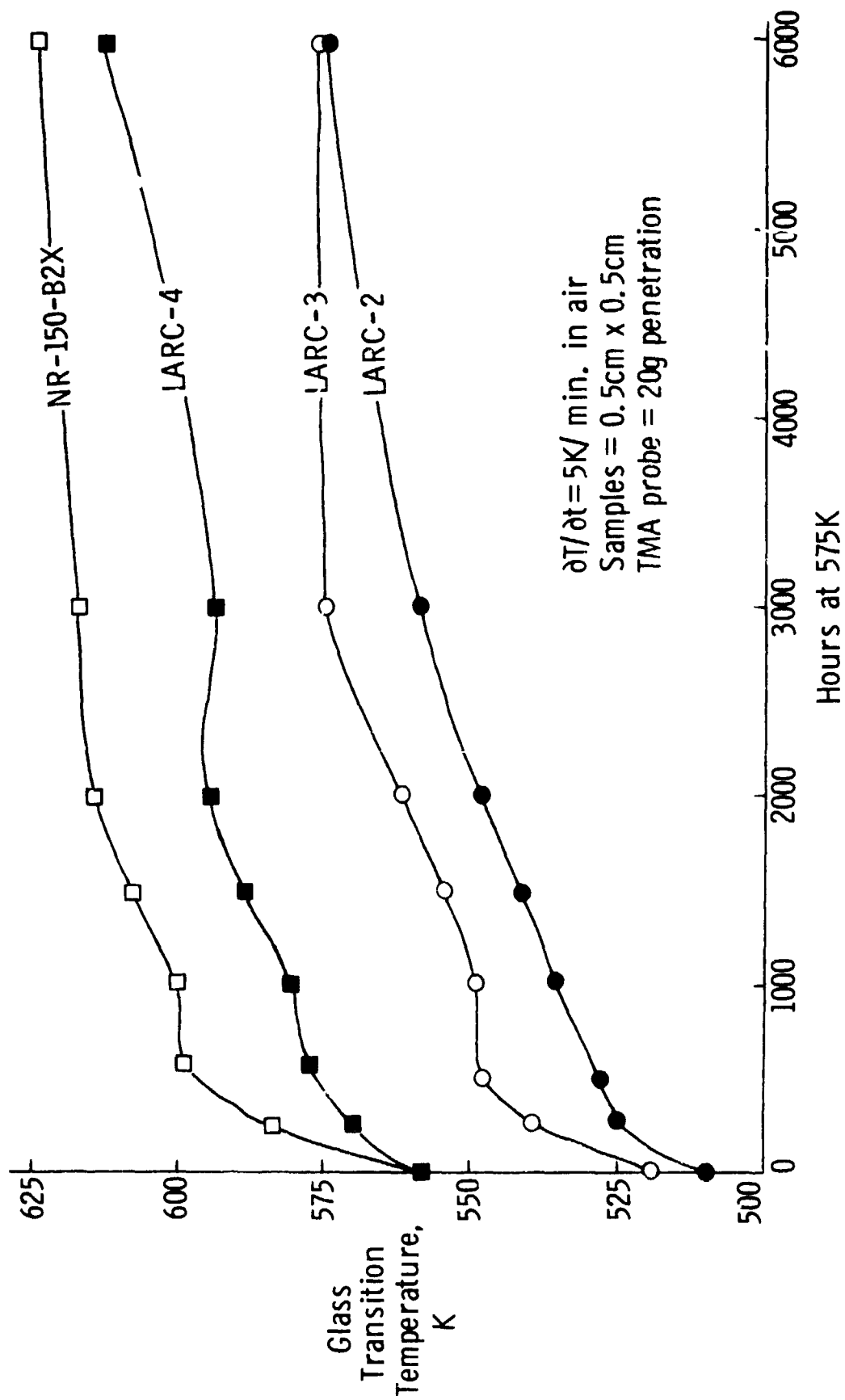


Figure 10. T_g s of Kapton/Kapton bondlines after aging at 575K in vacuum.

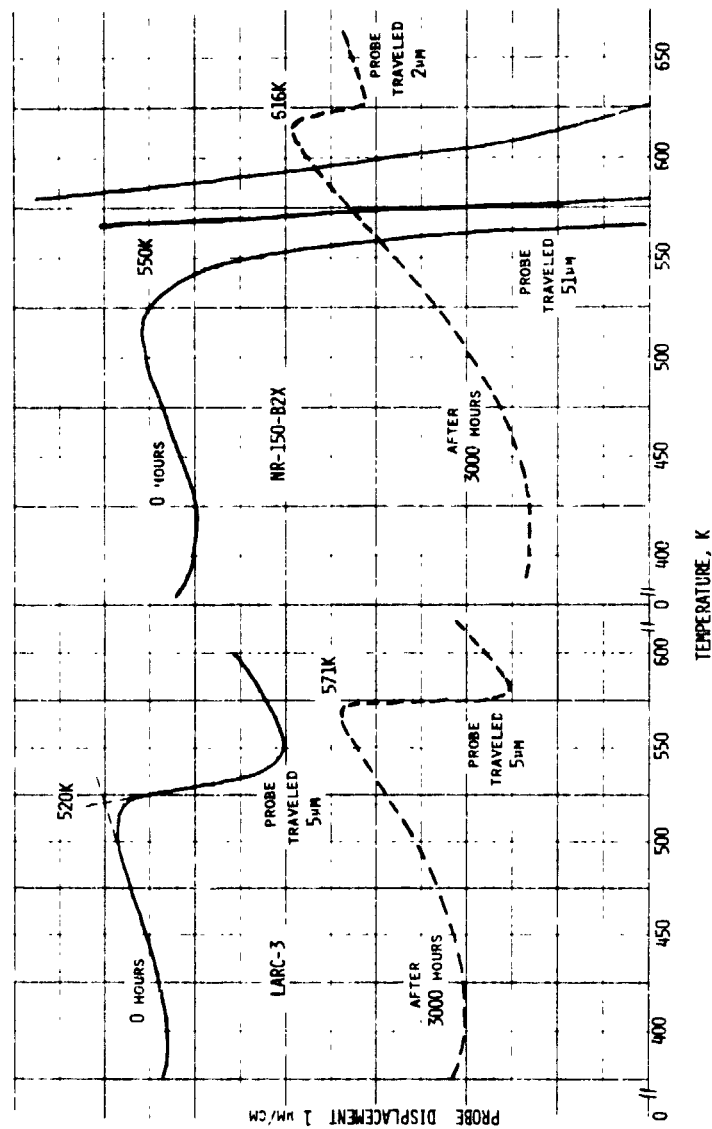


Figure 11. TMA curves of Kapton/Kapton bondlines.

1. Report No. NASA TM-81824		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle HIGH-TEMPERATURE ADHESIVES FOR BONDING POLYIMIDE FILM				5. Report Date May 1980	
				6. Performing Organization Code	
7. Author(s) Anne K. St. Clair, Wayne S. Slomp, and Terry L. St. Clair				8. Performing Organization Report No.	
9. Performing Organization Name and Address NASA Langley Research Center Hampton, VA 23665				10. Work Unit No 505-33-33-02	
				11. Contract or Grant No.	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546				13. Type of Report and Period Covered Technical Memorandum	
				14. Sponsoring Agency Code	
15. Supplementary Notes This document is an expanded version of a paper presented at the 23rd National SAMPE Symposium, Anaheim, CA, May 1978. Use of commercial products or names of manufacturers in this report does not constitute official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.					
16. Abstract Experimental polyimide resins have been developed and evaluated as potential high temperature adhesives for bonding Kapton polyimide film. Lap shear strengths of "Kapton"/"Kapton" bonds were obtained as a function of test temperature, adherend thickness, and long term aging at 575K (575°F) in vacuum. Glass transition temperatures of the polyimide/"Kapton" bondlines were monitored by thermomechanical analysis.					
17. Key Words (Suggested by Author(s)) Adhesives Polyimides Film Lap Shear Strength				18. Distribution Statement Unclassified - Unlimited Subject Categories 27, 02	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 26	
				22. Price* \$4.50	